Catalysis of Substitution at Rhodium(III)

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THE reactions of chlororhodium(III) complexes with nucleophiles are in general slow, so that convenient synthetic methods for rhodium(III) complexes are rare. One exception to this rule is the strong catalysis of nucleophilic substitution at rhodium(III) by two-electron reducing agents, and this effect has been exploited synthetically.[1] We now report some observations on the reaction of hydrazine with *trans*-dichlorobisethylenediamine-rhodium(III) salts, and some convenient synthetic extensions.

The reactions observed are:

$$\begin{tikzcd} trans\text{-}[\mathrm{Rh\,en_2Cl_2}]^{+} \arrow[r, "(a)"] & trans\text{-}[\mathrm{Rh\,en_2(N_2H_4)Cl}]^{2+} \arrow[d, "(b)"] \quad \text{(I)} \\ & trans\text{-}[\mathrm{Rh\,en_2(N_2H_4)_2}]^{3+} \quad \text{(II)} \end{tikzcd}$$

Reaction (a) is much faster (*ca.* 10^3 times) than reaction (b), so that by suitable choice of conditions (I) or (II) may be obtained pure. However, with hydrazinium salts, no apparent reaction occurs. Reaction (a) is also a great deal faster than the substitution[2] by ammonia and it is noted that as yet *trans*-$[\mathrm{Rh\,en_2(NH_3)_2}]^{3+}$ is unknown. The electronic spectra and other properties are consistent with the formulations given; (I) has $\lambda_{\max}$ 344, ϵ 125; ~290 mμ (160); {*cf.* *trans*-$[\mathrm{Rh\,en_2(NH_3)Cl}]^{2+}$,[2] $\lambda_{\max}$ 342 (95); 275 mμ (120)} and (II) has $\lambda_{\max}$ 298 mμ, ϵ 280; {*cf.* $[\mathrm{Rh\,en_3}]^{3+}$,[1,3] $\lambda_{\max}$ 299 (101); 253 mμ (110)}.

When (II) is heated with protonic acids, HX, the following very rapid reaction occurs (where X = Cl, Br, and I).

$$trans\text{-}[\mathrm{Rh\,en_2(N_2H_4)_2}]^{3+} \xrightarrow{(c)} trans\text{-}[\mathrm{Rh\,en_2X_2}]^{+}$$

Similarly (though less readily)

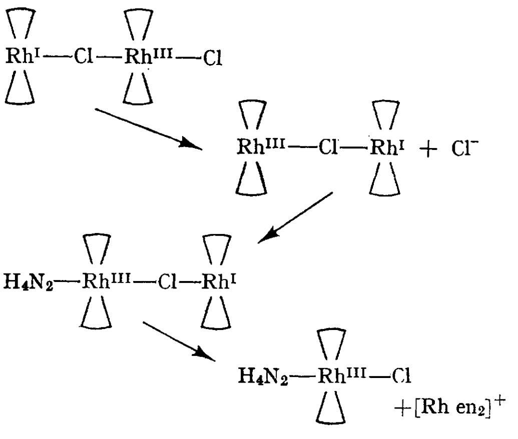
$$trans\text{-}[\mathrm{Rh\,en_2(N_2H_4)Cl}]^{2+} \xrightarrow{(d)} trans\text{-}[\mathrm{Rh\,en_2(X)Cl}]^{+}$$

These reactions require an acid as X^- ions alone will not serve. Thus, the catalysis by hydrazinium salts[4] of nucleophilic displacements on rhodium(III) depends on the reduction of the rhodium (III) and on the inability of the hydrazinium ion to act as a ligand. In this series, nucleophilic power is expressed by $N_2H_4 > Cl^- > N_2H_5^+$.

The mechanism envisaged in the catalysis, since the presence of an excess of Cl^- does not effect the rate of formation of (I), is

$$trans\text{-}[\mathrm{Rh\,en_2Cl_2}]^{+} \xrightarrow{\text{Slow}} [\mathrm{Rh\,en_2}]^{+}$$

$$[\mathrm{Rh\,en_2}]^{+} + trans\text{-}[\mathrm{Rh\,en_2Cl_2}]^{+} \longrightarrow$$



The postulated bridged intermediate is consistent with the catalysis by hydrazine of halide replacements observed by Pöe, Basolo, and Bounsall:[4]

trans-$[\mathrm{Rh\,en_2XY}] \longrightarrow$ *trans*-$[\mathrm{Rh\,en_2XZ}]$). The features observed here are similar to those[5] in some analogous platinum(IV)–platinum(II) catalyses; notably that chloride replacement (or exchange) is much slower in systems containing *trans*-Cl·M·N {*e.g.*, $[\mathrm{Pt(NH_3)_5Cl}]^{3+}$ or *trans*-$[\mathrm{Rh\,en_2(N_2H_4)Cl}]^{2+}$} than in *trans*-Cl·M·Cl {*e.g.*, $[\mathrm{Pt(NH_3)_4Cl_2}]^{2+}$ or *trans*-$[\mathrm{Rh\,en_2Cl_2}]^{2+}$}. The catalysed formation of *trans*-dichlorobisethylenerhodium(III) from the *trans*-dihydrazine complex in the presence of acid is reminiscent of the formation of *trans*-$[\mathrm{Pt(NH_3)_4Cl_2}]^{2+}$ from $[\mathrm{Pt(NH_3)_5Cl}]^{3+}$ with HCl in the presence of $[\mathrm{Pt(NH_3)_4}]^{2+}$.

A two-electron bridged activated complex mechanism was postulated[6] by Rund, Basolo, and

Pearson to account for the catalysis by ethanol of the formation of *trans*-dichlorotetrapyridinerhodium(III) from its constituents. This type of reduced intermediate seems likely to prove important in the chemistry of rhodium.

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